EFFECT OF PORE STRUCTURE ON CATALYTIC COAL LIQUEFACTION

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Introduction

Considerable evidence for pore diffusional limitations in coal liquefaction has been reported in the literature (1-10). In this research catalysts having different pore structures were prepared using two methods, impregnation and coextrusion. The pore structures were controlled either by a sintering technique or by using combustible fibers (7). The initial activity of prepared catalysts was evaluated in coal liquefaction reactions with tetralin solvent. A model describing the relation between catalyst surface area and catalyst activity was developed by assuming 1) that every pore perfectly communicates and has a cylindrical shape, 2) that the pellet catalyst has a simple bimodal pore size distribution and 3) that a single first-order reaction occurs in the diffusion controlled region. For simplicity, reactant molecular size also was assumed to be uniform.

Experimental Section

Catalyst Preparation. Catalysts were prepared using Catapal alumina (Vista Chemical Co.) and cellulose fiber (Avicel) using techniques similar to those used by Tischer (7). Ni and Mo were added by two methods: incipient wetness following calcination or prior to the extrusion process itself (coextrusion). Catalysts were presulfided prior to use. Catalysts were evaluated in 3/16 inch pellet form. The powder prepared by grinding the 3/16 inch pellets was also evaluated.

Catalyst Characterization. To measure the pore size distribution and apparent density of the extrudates, a Quantachrome Autoscan-33 porosimeter equipped with the Autoscan data reduction system was used. The maximum intrusion pressure of mercury was 33,000 psig, which corresponds to ca. 64 angstroms in pore diameter. Surface areas were obtained from a Quantasorb system using the multipoint BET method. Apparent density, macropore diameter and macropore volume of each catalyst were calculated from the mercury porosimeter data. True density, micropore diameter and total pore volume were obtained from a combination of pycnometer (water displacement), BET, and Hg porosimetry methods.

Coal Liquefaction. A horizontal welded tubing bomb microreactor of ca. 45 cc volume was used with the following reactants: 3 g Illinois #6 coal, 10 g tetralin, 1 g catalyst, and 1250 psig (cold) H_2. The reactor was agitated at 425 ^{o}C for 60 min in a fluidized bed sand bath. Liquefaction products were classified as gases, oils (pentane soluble), asphaltenes (benzene soluble), preasphaltenes (soluble in a mixture of 10 vol.% methanol and 90 vol.% methylene chloride), and IOM (insoluble organic matter). Solubility fractions were expressed on a solvent-free basis.

Results and Discussion

Characterization of Catalyst Pore Structure. Physical properties of laboratory prepared catalysts and supports are given in Table 1. A macropore is defined as a pore whose diameter exceeds 500 angstroms. Average pore diameters are calculated from the pore volume and BET surface area data by assuming cylindrical pores. Table 1 shows that the pore size distributions of unimodal 3/16" catalyst supports are dependent on the calcining temperature. As the calcining temperature increases, apparent density and average micropore diameter become larger, and surface area is reduced. This phenomenon results from a destruction of some micropores and reconstruction of macropores by a sintering process. Data for support D in Table 1 indicate that most micropores are destroyed and reoriented at high temperatures. Also, as shown in Table 1, the combustible fiber loading directly increases macropore volume and average macropore diameter.

Coal-Tetralin Reaction System. Catalysts shown in Table 1 were used in tetralin-coal reactions using both 3/16 inch pellets and their powder. The powder form of the catalysts, as shown in Table 2, gave the highest activity, indicating diffusional restrictions in the pellets. As shown in Table 2, calcining temperature had a direct effect on catalyst activity as evidenced by pentane-soluble oil yield. If the activity of the pellet catalysts is plotted versus the surface area, a maximal point in the catalyst activity exists. This interesting phenomenon results from a competition between the effective diffusivity and surface area. In a typical catalytic reaction of small molecules, an increase of surface area generally enhances catalyst activity. However, in a reaction of large molecules this increase can reduce the catalyst activity because of diffusional hindrance in the micropores. Thus, catalyst G, having the highest surface area of the unimodal catalysts, does not yield the most pentane soluble oils, due to the very small pore size and the hindered diffusion through these pores.

One way to increase pore accessibility without significantly reducing specific catalyst surface area is to introduce macropores. Using the technique of combustible fibers, we produced macroporous catalysts J,K, and L having high surface areas of 250-300 m^2/g. When compared to unimodal catalysts, the bimodal catalysts (J and K in Table 3) give an oils fraction slightly greater than the best unimodal catalyst (I) in Table 2. An increase of fiber loading from 20 to 40 wt% has little additional effect on the activity.

Development of Model. In order to analyze the above results we developed a catalyst model similar to that of Froment and Bischoff (11), i.e. a parallel pore cross linked model with perfectly communicating pores.

For a first order irreversible diffusion controlled catalytic reaction the reaction rate per pellet volume is

$$\begin{aligned} r_v &= k\, C_s\, \eta \\ &= k\, C_s / \phi \\ &= S_x\, (k\, D_e)^{1/2}\, C_s / V_p \\ &= (S_x\, k_s^{1/2} / V_p)\, (S_v D_e)^{1/2}\, C_s \end{aligned} \qquad (1)$$

where S_v is the surface area per pellet volume, and D_e is the effective diffusivity.

From a material balance in a batch reactor, we obtain

$$-\frac{d(C_s)}{dt} = r_v V_{cat} = r_g W_{cat} = (r_v / \rho_c) W_{cat} \qquad (2)$$

Solving eqs (1) and (2) together we obtain

$$\text{Ln}\ (C_s / C_{so}) = -k' t \qquad (3)$$

where k' is expressed as follows,

$$k' = \frac{S_x k_s^{1/2}}{V_p} \frac{V_{cat}}{} (S_v D_e)^{1/2} \qquad (4)$$

or

$$k' = \frac{S_x k_s^{1/2}}{V_p} \frac{W_{cat}}{} (S_g D_e / \rho_c)^{1/2} \qquad (5)$$

Equations 4 and 5 are useful for comparing catalyst activity in terms of physical properties such as porosity, density, pore sizes and pellet morphology. Equations (4) and (5) are most convenient when performing reactions using a constant catalyst volume or weight, respectively. In either case the first two terms remain constant if the catalyst shape and the amount of solvent are the same in each reaction.

As a very simple catalyst pore structure model, we adopt a model having only two sizes of cylindrical pores, denoted by radii R_1 and R_2. Define the total porosity, $\epsilon = \epsilon_1 + \epsilon_2$, where ϵ_1 and ϵ_2 are void fractions of micro (R_1)- and macro (R_2)-pores.

From the definition,

S_v = surface area of pores / volume of pellet

$$S_v = 2\ (\epsilon_1/R_1 + \epsilon_2/R_2) \qquad (6)$$

Introducing dimensionless variables $\lambda_i = R_m/R_i$ where R_m is the reactant molecule size (radius),

$$S_v = (2\ \epsilon/R_m)\ [(\epsilon_1/\epsilon)\ \lambda_1 + (\epsilon_2/\epsilon)\ \lambda_2] \qquad (7)$$

$$S_g = (2\ \epsilon/R_m/\rho_s)\ [(\epsilon_1/\epsilon)\ \lambda_1 + (\epsilon_2/\epsilon)\ \lambda_2]/(1 - \epsilon) \qquad (8)$$

In a dimensionless form,

$$\langle S_v \rangle = \epsilon\ [(\epsilon_1/\epsilon)\ \lambda_1 + (\epsilon_2/\epsilon)\ \lambda_2] \qquad (9)$$

$$\langle S_g \rangle = \epsilon/(1 - \epsilon)\ [(\epsilon_1/\epsilon)\ \lambda_1 + (\epsilon_2/\epsilon)\ \lambda_2] \qquad (10)$$

In the hindered diffusion regime, the effective diffusivity D_e is

$$D_e = (\epsilon\ D_m/\tau)\ [(\epsilon_1/\epsilon)\ K_{r1}\ K_{p1} + (\epsilon_2/\epsilon)\ K_{r2}\ K_{p2}] \quad (11)$$

where the frictional resistance, K_{ri} and partition factor, K_{pi} are expressed as follows (12).

$$K_{ri} = 1 - 2.104\ \lambda_i + 2.09\ \lambda_i^3 - 0.95\ \lambda_i^5 \quad (12)$$

$$K_{pi} = (1 - \lambda_i)^2 \quad (13)$$

Equation 11 assumes the tortuosity τ is not a function of pore size.

In a dimensionless form,

$$\langle D_e \rangle = \epsilon\ [(\epsilon_1/\epsilon)\ K_{r1}\ K_{p1} + (\epsilon_2/\epsilon)\ K_{r2}\ K_{p2}] \quad (14)$$

Define k_v and k_g from equations 4 and 5 as follows:

$$k_v = (S_v\ D_e)^{1/2} \quad (15)$$

$$k_g = (S_g\ D_e/\rho_c)^{1/2} \quad (16)$$

In a dimensionless form,

$$\langle k_v \rangle = \langle S_v \rangle^{1/2}\ \langle D_e \rangle^{1/2} \quad (17)$$

$$\langle k_g \rangle = \langle k_v \rangle/(1 - \epsilon) \quad (18)$$

Substituting equations 9 and 15 into equations 17 and 18 gives

$$\langle k_v \rangle = \epsilon\ [(\lambda_1\ \epsilon_1/\epsilon + \lambda_2\ \epsilon_2/\epsilon)\ x\ (\epsilon_1/\epsilon\ K_{r1}\ K_{p1} + \epsilon_2/\epsilon\ K_{r2}\ K_{p2})]^{1/2} \quad (19)$$

$$\langle k_g \rangle = \epsilon/(1 - \epsilon)\ [(\lambda_1\ \epsilon_1/\epsilon + \lambda_2\ \epsilon_2/\epsilon)\ x\ (\epsilon_1/\epsilon\ K_{r1}\ K_{p1} + \epsilon_2/\epsilon\ K_{r2}\ K_{p2})]^{1/2} \quad (20)$$

where $0 \leq \lambda_1 \leq 1$.

Model Application. The batch reactions conducted in this work were performed with constant catalyst weight and thus eq (20) is most useful for activity comparison. The major difficulty with direct application of eq (20) is that the reactant molecule radius R_m is unknown and, of course, has a wide distribution in coal reactions. To circumvent this problem, we utilize the fact that for a unimodal catalyst (ϵ_2=0), eq (20) has a maximum at λ_1=0.18 (12). This fact, together with the data of Table 2 showing an optimal micropore size of ca. 85 angstroms (catalyst I), can be used to define an approximate R_m of 15 angstroms. With this assumed value of R_m, <kg> can be computed from eq (20) using the catalyst properties in Table 1. The results of these calculations are given in Table 4.

Comparison of <kg> values with pentane soluble oils yield as given in Table 4 shows reasonable qualitative agreement, in view of the many approximations

made, e.g. first order reaction, single molecule size, etc. The bimodal catalysts have a slightly higher activity in terms of oils yield, however, the effect is not great. Model calculations indicate that a major advantage of the bimodal catalysts may appear later during catalyst deactivation when pore sizes are reduced due to coke and metal deposits, and reactant diffusion becomes more hindered compared to the fresh catalysts.

Nomenclature

C_s Reactant concentration, mole/cm^3
D_e Effective diffusivity, cm^2/s
D_m Molecular bulk diffusivity, cm^2/s
k Reaction rate constant in equation 1, 1/s
k' Reaction rate constant defined in equations 4 and 5, 1/s
k_g Reaction rate constant defined in equation 16, cm$^{7/2}$/g/s$^{1/2}$.
K_p Steric coefficient defined in equation 13
K_r Frictional drag coefficient defined in equation 12
k_s Surface reaction rate constant, cm/s
k_v Reaction rate constant defined in equation 15, cm^2/(g-s)$^{1/2}$
R Pore radius, cm
r_g Reaction rate based on catalyst weight, mole/g-cc
R_m molecule radius, cm
r_v Reaction rate based on catalyst volume, mole/cc-s
S_g Surface area per unit catalyst weight, cm^2/g
S_v Surface area per unit catalyst volume, 1/cm
S_x External surface area of pellet, cm^2/g
V Pore volume
V_p Pellet volume, cc/g
V_{cat} Catalyst volume per unit volume of liquid in reactor
W_{cat} Catalyst weight per unit volume of liquid in reactor

Greek Letters

ϵ Porosity
λ Ratio of molecule radius to pore radius
ρ_c Pellet density, g/cc
ρ_s Catalyst solid density, g/cc
τ Tortuosity
ϕ Thiele modulus
η Effectiveness factor

Subscripts

1 micropore
2 macropore
o initial
t total

Symbol

< > dimensionless group

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Table 1. Physical Properties of Catalysts

Catalyst Name	Calcining Condition (°C-hrs)	V_t (cc/g) H_g	V_t (cc/g) H_2O	V_1 (cc/g)	V_2 (cc/g)	S_g (m^2/g) H_g	S_g (m^2/g) BET	ρ_c (g/cc)	ρ_s (g/cc)	d_1 (angstroms)	d_2 (angstroms)
3/16" Supports used for Impregnation											
A	500 - 16	.43	.45	.45	a	240	220	1.30	3.09	81	a
B	750 - 16	.44	.43	.43	a	203	161	1.29	2.86	106	a
C	1000 - 16	.37	.34	.34	a	113	97	1.50	3.09	142	a
D	1200 - 16	.19	.20	.01	.19	5	3	1.98	3.32	500	1832
Coextruded 3/16" Catalyst: no fiber											
G	500 - 16	.03	.40	.39	a	11	287	1.47	3.50	55	a
I	580 - 16	.31	.42	.42	a	172	197	1.49	3.95	85	a
Coextruded 3/16" Catalyst: 20 wt% fiber											
J	500 - 16	.30	.47	.41	.06	98	301	1.29	3.27	56	1560
Coextruded 3/16" Catalyst: 40 wt% fiber											
K	500 - 16	.62	.80	.40	.40	110	272	.90	3.19	61	2348
L	580 - 16	.73	.81	.42	.39	156	258	.90	3.33	66	2253

Note:
- V_t: total pore volume measured by H_g or H_2O intrusion
- V_1: micropore volume from $V_t(H_2O) - V_2$
- V_2: macropore volume obtained from Hg porosimeter
- S_g: specific surface area by Hg porosimeter or BET analysis
- ρ_c: apparent density by Hg displacement
- ρ_s: true density obtained from H_2O pycnometry
- d_1: average micropore diameter $4V_1$/BET micropore area
- d_2: average macropore diameter $4V_2$/Hg macropore area
- a: no macropores

Table 2. Effect of Calcining Temperature on Product Distribution

Catalyst Name	Catalyst Shape	Sintering Temperature (°C)	Product Distribution (wt.%) Gases	Oils	Asphaltenes	Pre/Asphaltenes	IOM	Coal Conversion (wt%)
None	----	----	7	33	36	17	7	94
G	Pellets	500	6	41	23	14	16	84
	Powder	500	5	72	8	5	10	89
I	Pellets	580	6	53	20	9	12	88
	Powder	580	6	78	6	4	6	94
Impregnated on support C								
	pellets	1000	7	47	24	11	11	88
	powder	1000	6	73	13	4	4	95
Impregnated on support D								
	pellets	1200	6	34	36	15	9	90

Table 3. Effect of Fiber Loading on Product Distribution

Catalyst Name	Fiber Loading (wt%)	Catalyst Shape	Product Distribution (wt.%) Gases	Oils	Asphaltenes	Pre/Asphaltenes	IOM	Coal Conversion (wt%)
G	0	Pellets	6	41	23	14	16	84
		Powder	4	72	9	5	10	89
J	20	Pellets	5	55	19	9	12	87
		Powder	4	77	6	5	8	91
K	40	Pellets	6	57	16	8	13	87
		Powder	4	76	6	5	9	91

Table 4. Comparison of Model Catalyst Activity and Experimental Oil Yields

Catalyst	λ_1	λ_2	ϵ_1	ϵ_2	$\langle S_g \rangle$	$\langle k_g \rangle$	Oils Yield (wt%)
C	.11	a	.52	a	.119	.281	47
D	.03	.0082	.03	.37	.007	.065	34
G	.27	a	.58	a	.373	.360	41
I	.18	a	.62	a	.294	.452	53
J	.27	.0096	.54	.07	.376	.442	55
K	.25	.0064	.36	.36	.330	.730	57

Note: a) Catalyst contains no macropores.